Journal of Analytical Atomic Spectrometry

Automated On-line Preconcentration System for Electrothermal Atomic Absorption Spectrometry for the Determination of Copper and Molybdenum in Sea-water

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A flow injection accessory for electrothermal atomic absorption spectrometry was developed. The performance of the on-line preconcentration system was tested by determining Cu and Mo in sea-water. Calibration graphs constructed from the preconcentration of standards in 0.2% HNO_3 solution were used. On-line preconcentration is computer-controlled. A miniature Muromac A-1 resin column was inserted at the tip of the AS-60 autosampler arm. A modification of the AS-60 autosampler in the tubing line and circuit allowed either flow of the sample through the column or operation of the autosampler in the normal mode. Retention of the metal ions as complexes on the microcolumn was achieved by using Muromac A-1 as the chelating resin; 20% v/v HNO_3 was then used for elution. With a 198.6 µl sample loop, the throughput is 14 samples h^{-1}. Detection limits are 0.009 µg l^{-1} for Cu (606.9 µl sample loop) and 0.06 µg l^{-1} for Mo (50 µl sample loop and repeated four times). The accuracy of the method was confirmed by the analysis of certified reference saline waters.

Keywords: *Atomic absorption spectrometry; preconcentration; copper; molybdenum; sea-water*

Although electrothermal atomic absorption spectrometry (ETAAS) has very low detection limits for trace metals in aqueous solution,[1] the direct determination of trace metals in sea-water by ETAAS is difficult even with sophisticated background correction and chemical modification. This is due to the low concentrations and strong interference from the sample matrix. ETAAS with on-line sorbent extraction separation and preconcentration can solve the two problems mentioned above and lead to easy determination.

Sorbents used successfully as packing materials for on-line column preconcentration include chelating ion exchangers,[2–17] C_{18}-bonded silica gel, polymer sorbents, strongly basic anion exchangers, strongly acidic cation exchangers, and activated alumina.

Of these, column preconcentration using chelating resins as packing materials is simpler and less time consuming than the other options. Chelating resins such as Chelex-100,[2–6] Muromac A-1,[7–11] quinolin-8-ol immobilized on porous glass,[4,12–14] or on silica,[15,16] and poly(dithiocarbamate)[17] have been used for the enrichment of natural waters and biological materials.

A number of on-line chelating resin preconcentration systems for trace metal determinations have been reported.[2–17] In these systems, a controlled volume of sample is passed through a column containing a cationic resin, a chelating resin, or chelating groups immobilized on copolymer matrices that retain transition metal ions. After the sample loading step, the metal ions are stripped from the column with a suitable eluent and directly injected into the nebulizer of a flame atomic absorption or a plasma emission spectrometer for detection. On-line preconcentration systems are better than off-line batch preconcentration methods, because the former are more efficient, reproducible, easily automated, have low consumption of sample and reagent and low risk of contamination.[18] On-line flow injection column preconcentration in atomic spectrometry was reviewed by Fang *et al.*[19] The on-line column preconcentration systems with liquid delivery forced by air offer a number of advantages:[20–22] ease of automation; lower consumption of reagent; reduced risk of contamination; and the peristaltic pump can be used as the air drive. Beinrohr *et al.*[20] were the first to introduce air transportation of sample/eluent streams obtained from the air support of the atomic absorption spectrometer. Azeredo *et al.*[21] introduced the peristaltic pump as the air drive and integrated column preconcentration with ETAAS successfully by using a column packed with quinolin-8-ol immobilized on silica. Based on solid-phase extraction with C_{18} silica gel, Sperling and co-workers[23–26] modified the on-line flow injection system of a flame atomic absorption spectrometer to achieve feasible determinations with ETAAS.[23–26] We reported that trace metals (Cu, Cd, Pb) in sea-water could be determined using C_{18} silica gel and APDC with an automated on-line preconcentration system coupled with ETAAS.[27,28] Porta *et al.*[12] used different materials in the preconcentration column. Hirata and co-workers,[9,10] Taylor *et al.*[11] and Sung *et al.*[29] used Muromac A-1 chelating resin for on-line column preconcentration coupled with ICP-AES,[9] flame AAS,[10] ICP-MS[11] and ETAAS.[29]

In this work, some commercially available hardware and software components were used to automate the preconcentration procedure and decrease human intervention. A flow injection accessory for atomic spectrometry was developed; the rotation of the pump, the stop and go intervals, the actuation of the valves, and the time at which the thermal program of the atomic absorption measurement was started were controlled automatically by an IBM PC-compatible computer. A miniature Muromac A-1 column was inserted at the tip of the AS-60 autosampler arm. The functional group of Muromac A-1 is similar to that of Chelex-100 which contains the iminodiacetic acid[$-CH_2-N(CH_2COOH)_2$] group. The chelating ability of Muromac A-1 is comparable to that of quinolin-8-ol or Chelex-100.[9–11,29] Muromac A-1 resin is more highly purified and does not swell or shrink.[9] A modification of the AS-60 autosampler in the tubing line and circuit allowed either the flow of the sample through the column or the operation of the autosampler in the normal mode. The retention of the metal ions in the form of complexes on the microcolumn was

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achieved by using Muromac A-1 as the chelating resin; 20% v/v HNO_3 was then used for the elution. The accuracy of the method was confirmed by the analysis of certified reference saline waters.

EXPERIMENTAL

Reagents and Samples

High-purity water (18 MΩ cm) was prepared with a de-ionized water system (Milli-Q, Millipore). Nitric acid (Merck, suprapur grade) was purified by sub-boiling distillation. A 0.2% v/v HNO_3 solution, prepared from sub-boiled HNO_3, was further purified by passing it through the Muromac A-1 column. Commercial Cu and Mo standards (1000 mg l^{-1}, Merck) were used. The standard solution (1000 mg l^{-1}) of Mo or Cu was diluted to the desired concentration with purified HNO_3 solution (0.2%, v/v), which was also used as the conditioning and washing solution for the column in the preconcentration steps. A sea-water sample used for blank sea-water preparation was collected from coastal surface water near Hsinchu, Taiwan. The sea-water was filtered through a membrane filter (Millipore, 0.45 μm), acidified with HNO_3 and stored at 4 °C. Sea-water reference materials such as SLEW-1 (Estuarine Water), CASS-2 (Nearshore Seawater), and NASS-4 (Open Ocean Seawater) were obtained from the Marine Analytical Chemistry Standards Program of the National Research Council of Canada.

Blank Sea-water Preparation

Blank sea-water was prepared by passing the collected sea-water sample through a column packed with the Muromac A-1 resin. The residual Cu and Mo concentrations in the blank sea-water were less than 0.009 and 0.06 μg l^{-1}, respectively.

Microcolumn Preparation

The Muromac A-1 microcolumn, shown in Fig. 1, was prepared using a PTFE capillary tube of an AS-40 autosampler (2.5 cm × 0.94 mm id, Perkin-Elmer), packed with Muromac A-1 resin (Muromachi Chemicals, ≈7 μl, 100–200 mesh for Cu; ≈4 μl, 200–400 mesh for Mo). A resin with a larger mesh size and smaller volume was used for Mo determination to improve the recovery. Polyethylene frits (porosity 0.5 μm, taken from a Sep-Pak C_{18} cartridge, Waters) were fixed in both ends of the microcolumn.

Instrumentation

An atomic absorption spectrometer (Perkin-Elmer Model Zeeman 5100 PC), equipped with a graphite furnace (HGA-600), Zeeman-effect background correction, and a laboratory-built automated on-line preconcentration system were used. Pyrolytic graphite coated graphite tubes without a platform were used for Mo determination. For Cu determination, heated graphite atomizer (HGA) tubes with an integrated platform as opposed to HGA tubes with a L'vov platform were used. The main reason for using the integrated platform is that it is slightly larger than the standard L'vov platform and it is curved, allowing the loading of larger sample volumes, up to 50 μl, without difficulty.

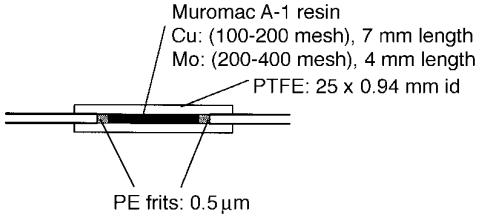

Fig. 1 Schematic diagram of the microcolumn assembly.

Preconcentration System

The major components and construction of the on-line ion-exchange preconcentration system are depicted schematically in Fig. 2(*a*) and (*b*). The smallest available sample loop volume in Fig. 2(*b*) is 135.1 μl. For Mo determination, the required sample volume for Mo is only 50 μl; hence, the system in Fig. 2(*b*) was modified to that shown in Fig. 2(*a*) and a 50 μl sample loop was used.

The microcolumn was mounted near the tip of the sampler capillary [Fig. 2(*a*) and (*b*)]. The solution was delivered by a peristaltic pump (Ismetac, MC-MS/CA4); this is a four-channel, variable-speed tubing pump. The four channels of the pump were connected as shown in Fig. 2(*a*) and (*b*) to draw air, sample, washing solution and elution solution, respectively. With this design, loading the sample, eluting and washing the column are carried out sequentially with only one variable-speed peristaltic pump.

The switch governing the pump rotation speed is computer-controlled. The design is as follows. In the Ismatec instruction manual, the peristaltic pump offers the user a set pump speed and flow rate either by using the push-button numerical controller on the front panel of the pump or by using an analog input signal to the pump, which accepts a 0–4.7 V dc, 0-10 V dc, 4–20 mA or 0–20 mA signal from a DB15 female connector on the back panel of the pump. The latter control method (using a 4–20 mA signal) is compatible with our computerized automated system design. For remote flow control, an adjustable flow controller was constructed using a digital potentiometer and three adjustable linearizing resistors (1 kΩ). Before starting the preconcentration procedure, the desired input current values are established by using a screwdriver to turn the adjust knob of the three adjustable linearizing resistors. The linearizing characteristic of the adjustable linearizing resistor *versus* the input current to the pump permits a linear increment of 0.12 mA per turn, and direct reading of the current from the liquid crystal display (LCD) of the digital potentiometer. Pump speeds used in different preconcentration steps (*e.g.*, washing, sample loading and elution steps) are switch selectable for three choices and controlled by computer.

It is necessary to meter accurately the volumes of the solutions used in sample loading, microcolumn washing, microcolumn conditioning and elution. This is effected by means of sampling loops. Three six-port rotary valves [Omnifit, V1–V3 in Fig. 2(*a*) and (*b*)] and two seven-port distribution valves [Omnifit, V4 and V5 in Fig. 2(*b*)] were used to construct the sampling loops in the preconcentration system. The lengths of the loops on the valves were chosen so as to obtain injected volumes between 50 and 600 μl. The volumes of the loops were calibrated by weighing. V1–V3 in Fig. 2(*a*) and (*b*) were actuated pneumatically by connecting the valves to the in-house high-pressure air line. V4 and V5 in Fig. 2(*b*) were actuated electrically by connecting the valves to stepper motors. The volumes of the sample loops in V1 (for column conditioning and washing) and V3 (for elution) are 103 and 50 μl, respectively. The volumes of the six sampling loops of V2, V4 and V5 [Fig. 2(*b*)] for sample loading cover the range 135.1–900 μl. These sampling loops are made with 0.3 and 0.8 mm id Teflon tubing. Three 30 ml poly(propylene) bottles (Nalgene) served as sample (standard or sea-water), washing (0.2% HNO_3) and elution (20% HNO_3) solution reservoirs. The connections between the pump, valves, column and reservoir bottles are made with 0.3 or 0.5 mm id Teflon tubing (Omnifit) and chemically inert type fittings (Omnifit).

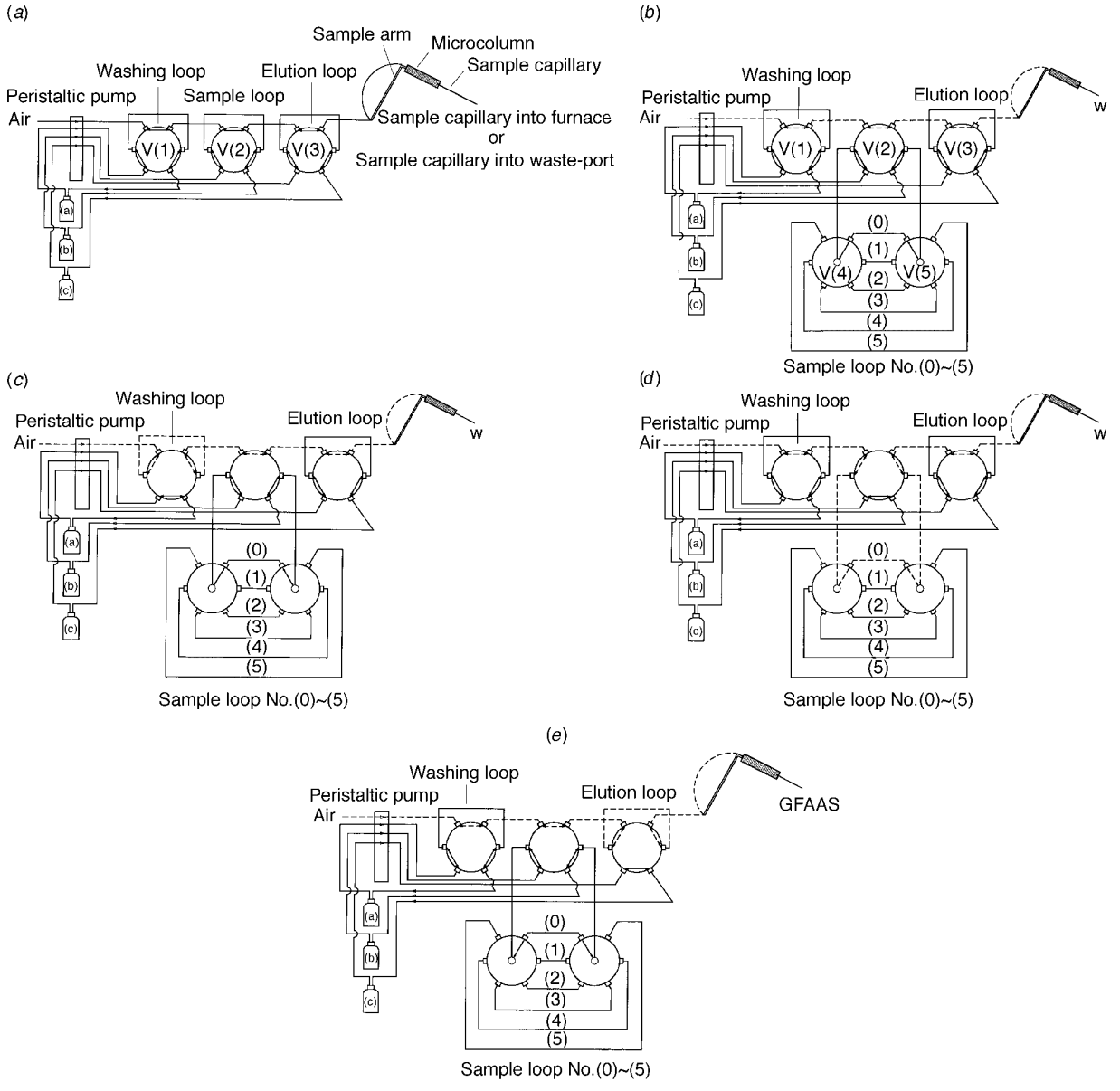

Fig. 2 Automated on-line preconcentration system.

An IBM PC-compatible computer was used to control various components of the preconcentration system. The control program was written in TURBO C. The rotation of the pump, stop and go intervals and the configuration of the valves are controlled by switching the dc power supply to these devices with solid-state relays activated by signals from I/O lines of the PC. The electrical communication between the experimental apparatus (valves, pump, *etc.*) and the computer was accomplished with an 8255-interface card (Yi Zhong Co.), which was installed in the computer. A simplified diagram of the system control circuit is shown in Fig. 3.

Preconcentration Procedure

The flow injection manifold and the sequence of its operation are shown in Fig. 2(*a*)–(*e*). The duration and function of each step are shown in Table 1. The conditions used here for the preconcentration of Cu and Mo from sea-water with Muromac A-1 were similar to those given elsewhere,[29] in which Muromac A-1 was also used to preconcentrate Cu and Mo from sea-water. The acidified sea-water samples (pH = 1.68–1.80) and aqueous standards (pH = 1.74) were preconcentrated directly without further adjustment of the sample pH. The six preconcentration steps using the automated system processes are as follows.

Step 1 for stand-by [Fig. 2(*b*)]: the PC configures the sample loops in V1, V2 and V3 to the 'load' position such that the washing, sample and elution solutions in the solution reservoirs are drawn through the sampling loops of the valves by the peristaltic pump until the loops are filled.

Step 2 for conditioning the microcolumn [Fig. 2(*c*)]: the PC configures V1 to the 'inject' position, and 0.2% HNO_3 solution in the sampling loop of V1 is delivered to the microcolumn by the peristaltic pump [flow as depicted by the broken lines in Fig. 2(*c*)]. After all the washing solution (0.2% HNO_3; 100 µl) in the loop has been drawn through the microcolumn, V1 is switched to the 'load' position.

Step 3 for sample loading on the microcolumn [Fig. 2(*d*)]: the PC configures V2 to the 'inject' position, and the standard or sample solution in the sampling loops of V2, V4 and/or V5

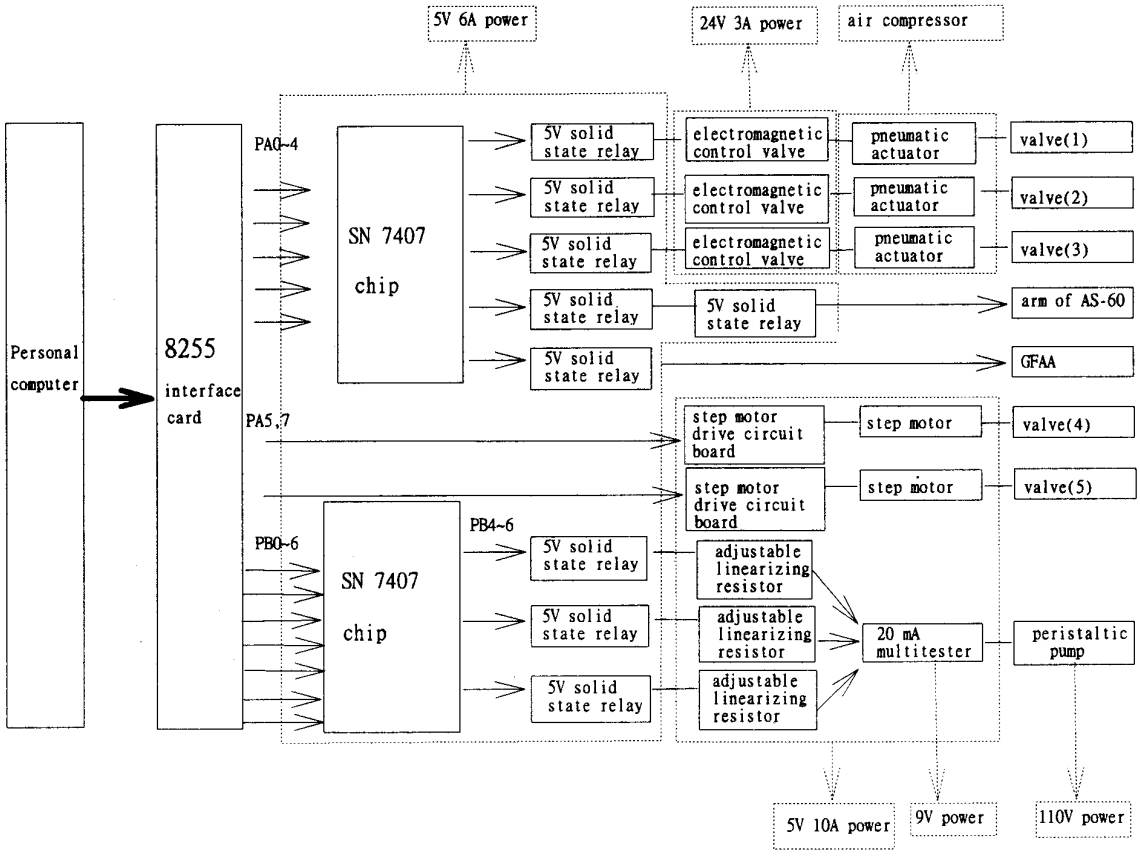

Fig. 3 Simplified diagram of preconcentration system circuit.

Table 1 Operating parameters and sequence of on-line flow injection automated preconcentration system for ETAAS using Muromac A-1 chelating resin

Step	Fig.*	Duration/s	Flow rate/μl s^{-1}	Valve position†	Purpose
1	(*b*)	15	5.0	Fill (1), (2), (3)	Fill the loops
2	(*c*)	50	5.0	Inject (1) Fill (2), (3)	Condition column
3	(*d*)	[76, 90, 116, 137, 181, 263]‡	4.5	Inject (2) Fill (1), (3)	Load sample
4	(*c*)	50	5.0	Inject (3) Fill (1), (2)	Wash sample matrix in column
5	(*e*)	55	1.6	Inject (3) Fill (1), (2)	Elute analyte into graphite tube
6	(*b*) (*e*)	15 55	5.0 1.6	Fill (1), (2), (3) Inject (3) Fill (1), (2)	Fill the loops Elute residual analyte to waste

* See Fig. 2.
† (1), (2) and (3) are the valves V1, V2 and V3 in Fig. 2(*a*) and (*b*), respectively.
‡ Correspond to volume (μl) of sample loop as follows: 135.1, 198.6, 311.9, 406.9, 606.9, 976.0.

is delivered to the microcolumn by the peristaltic pump [flow as depicted by the broken lines in Fig. 2(*d*)]. After all the standard or sample solution in the sampling loop has been delivered to the microcolumn, V2 is switched to the 'load' position; the position of V4 and V5 is converted to 'zero'.

Step 4 for washing the microcolumn [Fig. 2(*c*)]: the process is the same as for step 2.

Step 5 for microcolumn elution [Fig. 2(*e*)]: the PC configures the AS-60 autosampler arm to the 'inject' position (the tip of the sampler capillary is inserted into the dosing hole of the graphite tube), which is held in place during the introduction and retracted at the end of the step. The PC then configures V3 to the 'inject' position, and 20% HNO_3 solution in the sampling loop of V3 (50 μl) is delivered to the microcolumn by the peristaltic pump [flow as depicted by the broken lines in Fig. 2(*e*)], and the effluent from the microcolumn containing the trace metals of interest is directed into the graphite tube. After all the elution solution (20% HNO_3; 50 μl) in the loop has been drawn through the microcolumn, the position of the AS-60 autosampler arm is switched to 'waste' and V3 is switched to the 'load' position. Simultaneously, the thermal measuring cycle of the furnace is initiated by means of the PC. The transient absorbance was recorded and quantified by peak area measurement.

Step 6 for cleaning the microcolumn [Fig. 2(*b*) and (*e*)]: after step 5 (elution), the PC configures the system as in Fig. 2(*b*) in order to refill the elution loop of V3 (50 μl). Next, the PC configures the system as in Fig. 2(*e*) to elute the residual metal retained on the microcolumn to waste.

A complete cycle of preconcentration and eluate introduc-

Table 2 Test of the relationship between flow rate *versus* the input current to the pump

Experimental conditions*	Calibration range†	Equation	Correlation coefficient
A	$x = 4.80–9.20$: $y = 2.07–7.09$	$y = 1.0584x - 2.9996$	0.9983
B	$x = 4.20–5.80$: $y = 2.60–7.61$	$y = 3.0963x - 10.3999$	0.9995
C	$x = 4.10–5.00$: $y = 3.10–7.98$	$y = 5.3789x - 18.8705$	0.9987

* A: Using 0.89 mm id pump tubing; B and C: both using 1.33 mm id pump tubing, but with different tubing occlusion.
† x: Electric current input to pump (mA); y: flow rate through microcolumn (μl s^{-1}); microcolumn: 100–200 mesh and 7.0 mm length.

tion, consisting of six steps, takes 260 s with a sample loading period of 90 s (corresponding to a 198.6 μl volume of the sample loop).

RESULTS AND DISCUSSION

Test of Flow Rate Control

The flow rate was controlled by adjusting the input current to the pump. A test of flow rate control, in terms of the relationship between flow rate *versus* the input current to the pump, was performed. Table 2 shows that the calibration graphs were reasonably linear within the range of interest.

Graphite Furnace Heating Program

The effects of ashing temperature on the atomic absorbance and background absorbance are shown in Figs. 4 and 5; the atomization temperature was 2300 °C for Cu and 2650 °C for Mo. The sea-water matrix had been removed effectively through the preconcentration steps; therefore, varying the ashing temperature (Cu: 300–1400 °C; Mo: 300–1800 °C) has little effect on the atomization and background signals. The background signals of Cu and Mo remained in the ranges 0.052–0.056 (most of the background signal arises from overlapping Zeeman splitting components of the analyte line) and 0.001–0.005, respectively. Ashing temperatures of 1400 and 1800 °C were chosen for Cu and Mo, respectively.

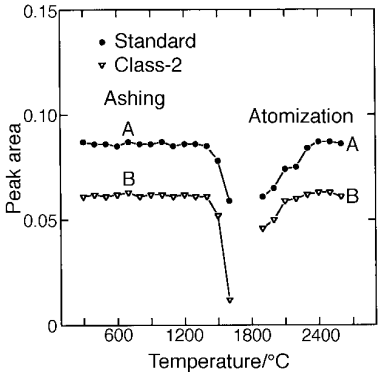

Fig. 4 Ashing and atomization curves for Cu. An atomization temperature of 2300 °C was used to establish the ashing curve and an ashing temperature of 1400 °C was used for the atomization curve. A, 50 μl of 20% HNO_3 eluate after preconcentration of aqueous standard (1 μg l^{-1} Cu) with a 198.6 μl loop. B, 50 μl of 20% HNO_3 eluate after preconcentration of CASS-2 Sea-water with a 198.6 μl loop.

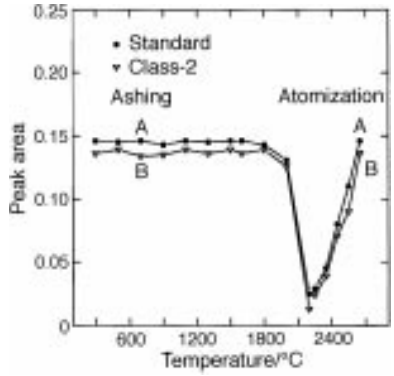

Fig. 5 Ashing and atomization curves for Mo. An atomization temperature of 2650 °C was used to establish the ashing curve and an ashing temperature of 1800 °C was used for the atomization curve. A, 50 μl of 20% HNO_3 eluate after preconcentration of aqueous standard (10 μg l^{-1} Mo) with a 50 μl loop. B, 50 μl of 20% HNO_3 eluate after preconcentration of CASS-2 Sea-water with a 50 μl loop.

For Cu, the effect of atomization temperature on the absorption signal is shown in Fig. 4; the absorption signal remained constant over the range 2300–2600 °C. An atomization temperature of 2300 °C for Cu was selected. For Mo, the effect of atomization temperature on the absorption signal is shown in Fig. 5; the absorption signal of Mo increases with increasing atomization temperature (2000–2650 °C). An atomization temperature of 2650 °C for Mo was chosen for maximum sensitivity.

The temperature programs for Cu and Mo determinations are shown in Table 3.

Effect of Sample Loading Flow Rate on Relative Recovery

The effect of sample loading flow rate on relative recovery was evaluated by extracting the heavy metal ions from an aqueous standard at flow rates varying over the range 2.07–5.61 μl s^{-1} for Cu and 2.20–5.82 μl s^{-1} for Mo. The results are shown in Fig. 6. The data for Cu and Mo were normalized to the values at flow rates of 2.07 and 2.20 μl s^{-1}, respectively. The sample loading rate over the range 2.07–5.61 μl s^{-1} did not affect the

Table 3 Graphite furnace temperature program

	Cu			Mo		
	Temperature/°C	Ramp/s	Hold/s	Temperature/°C	Ramp/s	Hold/s
Drying	150	1	70	150	1	70
Ashing	1300	5	20	1600	1	20
Cooling	20	1	15	20	1	15
Atomization	2300	0	5	2650	0	5
Clean-out	2650	1	5	2650	1	5
	20	1	5	20	1	5
	2650	1	5	2650	1	5

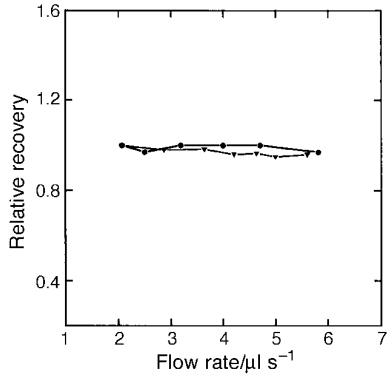

Fig. 6 Effect of sample loading flow rate on relative recovery for extracting the heavy metal ions from an aqueous standard (Cu: 2 μg l^{-1}, 134.8 μl loop; Mo: 10 μg l^{-1}, 50 μl loop).

relative recovery significantly. A sample loading flow rate of 5.0 μl s^{-1} was selected for Cu and Mo determination.

Sea-water Analysis

The slopes of calibration graphs established from the preconcentration of standards prepared in 0.2% HNO_3 solution and in blank sea-water were almost identical (shown in Table 4); hence Cu and Mo in sea-water can be determined using calibration graphs constructed from the preconcentration of standards in 0.2% HNO_3 solution.

The accuracy of the method was examined by the determination of Cu and Mo in certified reference saline waters (SLEW-1, CASS-2 and NASS-4). Table 5 shows that the method provides analytical results within the ranges of the certified values.

Table 4 Calibration graph constructed from preconcentration of standards (Cu and Mo prepared in 0.2% HNO_3 solution and blank sea-water, respectively)

Element	Equation*	Correlation coefficient	Matrix of standard
Cu†	$y=0.0060x+0.00035$	0.9987	0.2% HNO_3 solution
	$y=0.0060x+0.00033$	0.9986	Blank sea-water
Mo‡	$y=0.0158x-0.0009$	0.9984	0.2% HNO_3 solution
	$y=0.0159x-0.0010$	0.9988	Blank sea-water

* y and x are integrated absorbances and metal concentrations (μg l^{-1}), respectively.
† Cu standard solution (1–2 μg l^{-1}, 135.1–311.9 μl).
‡ Mo standard solution (5–10 μg l^{-1}, 50 μl).

Table 5 Trace element determination in sea-water reference materials using on-line preconcentration and ETAAS

	Cu/μg l^{-1}		Mo/μg l^{-1}	
Sample	Certified	Found*,†	Certified	Found*,‡
SLEW-1	1.76±0.09	1.82±0.0006	—	4.10±0.08
CASS-2	0.675±0.039	0.675±0.007	9.01±0.28	9.05±0.09
NASS-4	0.228±0.011	0.224±0.0017	8.84±0.60	8.29±0.16

* Mean and standard deviation of triplicate runs.
† Sea-water sample volume: SLEW-1 (100 μl), CASS-2 (198.8 μl), NASS-4 (406.1 μl).
‡ Sea-water sample volume: SLEW-1 (50 μl), CASS-2 (50 μl), NASS-4 (50 μl).

Detection Limit and Precision

The method detection limits, based on three times the standard deviation of eight replicate measurements of blank sea-water using different sample loop volumes, are shown in Table 6. The sample volume for Cu [Fig. 2(*b*)] is adjusted by selecting the sample loop. The sample volume for Mo [Fig. 2(*e*)] is adjusted with a multi-injection mode. The multi-injection mode allows the sample solution to be repeatedly loaded and injected on to the microcolumn for the number of times specified by the user in the control program. The technique improves the detection limit and the dynamic range of the sample loop. The detection limit of the method decreased with increasing sample volume.

The average integrated absorbance obtained with the preconcentration procedure for eight replicate measurements of CASS-2 (198.6 μl) is 0.063±0.002, and the relative standard deviation is 3.8%. The results show that this system can execute a series of preconcentration and determination procedures with high precision. The system using a column packed with Muromac A-1 chelating resin (4–7 μl) can be used for over 150 preconcentration cycles without any noticeable deterioration in performance.

CONCLUSION

Although on-line preconcentration systems such as the FIA 200 (Perkin-Elmer) are commercially available, our inexpensive laboratory-built preconcentration system (which cost US $2870) coupled with a Muromac A-1 microcolumn performed well and is fully automated. The laboratory-built preconcentration system, which is completely computer-controlled, not only enables instrument operation to be preprogrammed rather than performed manually, but also permits rapid reprogramming when it is necessary to change the preconcentration procedure for the system.

We thank the National Science Council of the Republic of China for grants (NSC-85–2113-M007–028 and NSC-84–2621-M007–001ZA) in support of this work.

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Table 6 Detection limits

Cu			Mo		
Sample volume/ μl	Detection limit/ μg l^{-1}	Enrichment factor*	Sample volume/ μl	Detection limit/ μg l^{-1}	Enrichment factor*
135.1	0.0345	3	50	0.24	1
198.6	0.0218	4	100	0.14	2
311.9	0.0149	6	150	0.08	3
406.9	0.0131	8	200	0.06	4
606.9	0.0088	12			

* Compared with direct introduction of 50 μl aqueous solution.

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Paper 7/01657C
Received March 10, 1997
Accepted April 22, 1997